DISLODGEABLE FOLIAR RESIDUES OF CHLOROTHALONIL (BRAVO^{R}) ON ROW CROPS IN CALIFORNIA DURING 1987

By

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SUMMARY

The fungicide chlorothalonil (tetrachloroisophthalonitrile) is currently in the SB 950 Risk Assessment Review process because of carcinogenicity in laboratory animals. The Worker Health and Safety Branch collected foliage samples from fields of cabbage, broccoli, cauliflower, tomato and celery grown in California in 1987 after applications of chlorothalonil. Samples were collected at intervals post-application to characterize field residues. Sampling continued until the crops were harvested or until no detectable residue was present. Chlorothalonil foliar dislodgeable residues on Day 1 post-application ranged from 0.46 ug/cm^2 on cabbage to 6.96 ug/cm^2 on celery. Results of non-linear regression analysis showed half lives varied from 1 to 12 days post application. Estimates of worker exposure using the Zweig-Popendorf model were also performed on the residue values at the expiration of the preharvest interval. These estimates showed an exposure range of 0.5 mg/person/day at one day for cabbage to 115 mg/person/day for celery at seven days. Dermal exposure monitoring (two studies) demonstrated exposure during tomato harvest to be about 40-50 mg/person/day.

INTRODUCTION

Chlorothalonil (tetrachloroisophthalonitrile) is a broad spectrum fungicide available in Category I, II and III. Bravo^{R} (chlorothalonil) is formulated as a wettable powder, flowable liquid and as a dust(1). The formulations used in this study were Bravo W-75 (wettable powder) and Bravo 500 (flowable liquid). It is used for the control of numerous plant pathogens and mildews. Chlorothalonil has an oral LD_{50} (rats) of >16,000 mg/kg and a dermal LD50 (rabbits) of >14,000 mg/kg. Chlorothalonil is a mild skin irritant and is possibly a skin sensitizer. Chlorothalonil is also a severe eye irritant which causes corneal damage and corrosion (2). Some individuals have complained that exposure to chlorothalonil produces allergic symptoms.

Approximately 384,020 pounds (active ingredient) of chlorothalonil were sold in California in 1985(3). For the years 1982-1985 there have been 17 reported pesticide illness reports where chlorothalonil was the causal pesticide. Eye and skin injuries were the highest percentage of these cases probably due to the high irritant effect of this compound (2). The Worker Health and Safety Branch collected foliage samples from various row crops (at different time intervals) after applications of chlorothalonil to characterize field residues. These data would be used to develop an initial exposure assessment for field workers harvesting chlorothalonil treated celery and tomatoes.

METHODS AND MATERIALS

With the assistance of the County Agricultural Commissioners' staff, cooperation was obtained from growers and pest control operators who would be using chlorothalonil during the 1987 season. The fields in our study were selected at random. One cauliflower and two broccoli fields were located in Monterey County and sampled during May and June. During this same time of year, the four celery fields were sampled in Orange County. Three cabbage fields in Santa Barbara County were sampled in July and August. The tomato fields in Colusa County were sampled in August and September. All applications to the celery fields were delivered by ground equipment, all other fields were applied by aerial applicators. Application rates ranged from one to three pounds of active ingredient in 10-100 gallons of water per acre. See Table I for application information for all fields by crop.

Weather conditions for Santa Barbara and the Salinas Valley averaged highs of 77°F. and lows of 51°F. The only rainfall was recorded during May (0.19 inches) in the Salinas Valley. Average temperatures in Orange County ranged from 82°F. to 55°F. and in Colusa County it was hot with the high averaging 102°F. and a low of 53°F. Cabbage, cauliflower and broccoli fields were sprinkler irrigated. The celery and tomato fields were furrow irrigated.

Once a field was selected, it was divided into three areas. Non-adjacent rows were designated A, B and C. Each row sampled was marked at the beginning of the row and at the location of the first and last sampled plant in that row. In Row A sampling commenced on the plant approximately 25 meters into the row and on the right. In Row B sampling began near the middle of the row, and in Row C sampling began such that the turnaround

point on that sampling subset to be 25 meters from the opposite end.

Eight to ten plants were sampled from the right on entering the field and eight to ten plants were punched from the left on exiting the row. The areas sampled represented a diagonal across the field. Punches were taken from leaves presenting the greatest area of exposed surface.

Foliage disc samples were collected using a 2.54 cm (inch) diameter Birkestrand leaf punch. On the day of the applications, pre-application samples were collected whenever possible. Post-application sampling intervals varied per field. Samples were collected between 1-28 days post-application. Sampling continued until the crops were harvested or until no detectable residue was present.

One complete sample consisted of 15-20 foliage discs from each of the three sections for a total of 45-60 leaf discs. After collection, all samples were sealed with aluminum foil, capped, stored on ice and extracted within 24 hours for later analysis of chlorothalonil dislodgeable residue by the Sacramento Chemistry Laboratory Services Unit. Dislodgeable residues were removed by rinsing the leaf surfaces using a water-surfactant solution, then extracted from the aqueous solution with ethyl acetate. Samples were analyzed by gas chromatography.

Nonlinear interative least square regression techniques were employed to examine both initial deposition and decay rates in the study. Initial analysis will assume a first-order exponential decay model which takes the following functional form:

$$y \text{ in } ug/cm^2 = B_0 e^{B_1 t}$$

where B_0 = initial deposition
B_1 = first order decay rate constant
and t = time since application

The exponential model was chosen so that the first order half-life could be estimated. The half-life in an indicator of the rate of dissipation of a compound once it is applied to a crop (8).

RESULTS

Individual fields were analyzed assuming a first order exponential decay model (4). The results are reported in Table II. Half lives ranged from one day post application on cabbage to twelve days on celery. Data from fields 3, 101, 103 and 5000 were not analyzed because they were only sampled on day three and were not sampled early enough or sampling was not carried out far enough. Mean and standard deviation for all the fields are reported in Table III. Results ranged from 0.46 ug/cm^2 on cabbage to 6.96 ug/cm^2 on celery on day one post-application. Analytical results for chlorothalonil treated fields are given in the Appendix along with the mean and the standard deviation in Table 3. Factors contributing to the variability of results among the fields include four different locations in the state, five different crops, two types of application equipment, two application rates, three different dilutions rates, two methods of irrigation and incomplete data for specific sample days. No additional analysis was performed because of the number of variables.

DISCUSSION

Zweig and Popendorf developed a model to estimate the relationship between workers' dermal exposure measurements and dislodgeable foliar residue (4). Using their methods and an average chlorothalonil dislodgeable residue level for a specific sampling day we can estimate dermal exposure from our data. Estimates assume an eight hour workday.

Crop	Days Post Application	Average Dislodgeable Residue (ug/cm^2)	Zweig-Popendorf (mg/person/day)
Cabbage	1	0.009	0.363
Broccoli	1	1.63	65.12
Cauliflower	1	1.90	76
Tomatoes	8	1.06	42.35
Celery	7	2.89	115.6

Calculated by: ug/cm^2 x 5000 cm^2/hr x hr/day x mg/1000 ug. Residues at eight days were used for tomatoes because it was the earliest day sampled in all three fields. Seven-day residue levels were used for celery to comply with label statements, "Do not apply within 7 days of harvest," and workers would not be expected to enter fields before this day.

Two dermal exposure studies of tomato harvest workers were available for comparison (6),(7). The study by SDS Biotech Corporation involved 10 male workers hand harvesting tomatoes at varying intervals of days after the last of four biweekly spray applications of Bravo 500 at 2.09 pounds active ingredient per 100 gallons of water per acre. Each worker picked tomatoes for 8 hours/day for 4 days except on the first day they worked 4.5 hours. Harvesters wearing short sleeves, and no hats or gloves had an average exposure of 51 mg/person/day. In their study the average deposit of dislodgeable chlorothalonil on tomato leaves 7 days after application was 3.04 ug/cm^2 compared to our average of 1.06 $ug/cm^2 \pm 0.69$ ug/cm^2 eight days after application.

In the other worker exposure study conducted by this Branch (7) involving 26 workers picking bush tomatoes five days after application of 1.5 pounds active ingredient per acre in 10 gallons of water five and thirty-three days before harvest, the maximum dermal exposure level calculated was 42.9 mg/person/day. This group of workers did not wear gloves; handrinses, socks and long-sleeve undershirts were used to measure worker exposure. The mean dislodgeable leaf residue was 3.05 ug/cm^2, again three times the 1.06 ug/cm^2 value used in the Zweig-Popendorf calculation. We found no other worker exposure studies for comparison on any of the other crops.

Since residue levels in the two studies involving direct exposure measurements on harvest workers were three times what we found here, but gave the same worker exposure measurements, the Zweig-Popendorf model estimates are on the high end of the exposure range. Assuming the residue

levels from this study are representative of the crops sampled, the Zweig-Popendorf model could be used for estimation of worker exposure.

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Table I

Application Information

Crop	Field(s)	Pesticide Product	Active Ingredient Pound Per Acre	Dilution Rate Gallons of Water Per Acre
Cabbage	1, 2	Bravo W-75*	1	20
Cabbage	3	Bravo W-75	1	20
Broccoli	10, 19	Bravo 500**	1	20
Cauliflower	18	Bravo 500	1	20
Tomatoes	101, 102, 103	Bravo 500	2.25	10
Celery	3000, 5000 5001, 9000	Bravo W-75	2.25	100

* Bravo W-75, E.P.A. 50534-23-AA (0.75 pounds active ingredient per pound of formulated product).

** Bravo 500, E.P.A. 50534-8AA (4.17 pounds active ingredient per gallon of formulated product).

Table II

Results From Non-Linear Regression Analyses

Field	Initial Deposition Estimate (ug/cm^2)	Predicted Residue Estimate at Day 14 (ug/cm^2)	Estimated Decay Rate Constant	Half-Life (Days)
1,2	1.01 -0.42, 2.44	0.00020	-0.61 -0.75, 1.96	1.1
10	1.018 0.792, 1.244	0.24	-0.104 0.040, 0.167	6.7
19	3.21 2.433, 3.994	0.99	-0.084 0.0126, 0.156	8.3
18	2.68 2.248, 3.106	0.38	-0.14 0.073, 0.204	5.0
3000	5.57 5.00, 6.14	0.26	-0.22 0.15, 0.30	3.2
5001	6.09 5.07, 7.10	3.02	-0.0542 0.03, 0.08	12.8
9000	5.53 4.65, 6.41	1.06	-0.0926 -0.03, 0.13	7.5

Table III

Mean and Standard Deviation Foliage Dislodgeable Residues for Chlorothalonil in Micrograms Per Square Centimeter

Crop/ County	Field Number	Sampling Interval	Mean	Standard Deviation
Cabbage Santa Barbara	1	Day 1	0.55	0.15
		Day 7	0.013	0.005
		Day 14	0.03	0.01
		Day 19	0.12	0.04
		Day 21	0.11	0.06
		Day 28	0.03	0.01
Cabbage Santa Barbara	2	Day 1	0.55	0.15
		Day 7	0.001	0.0007
		Day 14	0.03	0.01
		Day 19	0.12	0.03
		Day 21	0.11	0.06
		Day 28	0.03	0.01
Cabbage Santa Barbara	3	Day 1	0.77	0.12
		Day 7	0.013	0.005
		Day 14	0.001	0.0006
Broccoli Monterey	10	6 Hours	0.04	0.46
		Day 1	1.10	0.01
		Day 5	0.8	0.21
		Day 14	0.063	0.002
		Day 26	0.033	0.02
Broccoli Monterey	19	6 Hours	4.08	0.71
		Day 1	1.98	0.23
		Day 2	2.46	0.77
		Day 7	2.43	0.30
		Day 14	0.85	0.22
Cauliflower Monterey	18	6 Hours	2.57	0.24
		Day 1	1.90	0.67
		Day 2	2.56	0.47
		Day 7	1.01	0.25
		Day 14	0.16	0.12
		Day 28	0.06	0.08
Tomatoes Colusa	101	Day 8	0.92	0.26
		Day 14	-	-
		Day 21	-	-

Table III (Continued)

Crop/ County	Field Number	Sampling Interval	Mean	Standard Deviation
Tomatoes Colusa	102	Day 8	1.84	0.37
		Day 14	0.77	0.35
		Day 21	-	-
Tomatoes Colusa	103	Day 3	0.49	0.46
		Day 6	1.22	1.50
		Day 8	0.42	0.36
Celery Orange	3000	Pre-App	0.001	0.0002
		2 Hours	5.26	0.92
		Day 1	4.77	0.71
		Day 7	2.85	2.16
		Day 13	-	-
		Day 21	0.30	0.21
		Day 28	N.D.	-
Celery Orange	5000	Pre-App	1.45	0.41
		2 Hours	3.66	0.62
		Day 1	4.4	1.21
		Day 7	2.93	0.25
Celery Orange	5001	Pre-App	2.93	0.25
		2 Hours	5.63	0
		Day 1	-	-
		Day 5	4.98	1.09
		Day 14	2.64	0.62
Celery Orange	9000	Pre-App	0.67	0.17
		2 Hours	4.44	0.73
		Day 1	6.14	0.87
		Day 5	3.6	1.18
		Day 14	1.76	0.73
		Day 21	0.23	0.06
		Day 28	0.15	0.02

(-) Dash marks indicate only one data point.
N.D. - None detected, below 0.00038 ug/cm^2 minimum detectable level.

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Appendix

Foliar Dislodgeable Residues for Chlorothalonil Data From Samples Taken in 1987, all Residues Shown in Micrograms Per Square Centimeter

Crop/ County	Field Number	Sampling Interval	Replicate A	Replicate B	Replicate C
Cabbage Santa Barbara	1	Day 1	0.4600	0.7200	0.4700
		Day 7	0.0180	0.0130	0.0080
		Day 14	0.0160	0.0420	0.0300
		Day 19	0.1200	0.1600	0.0930
		Day 21	0.1700	0.0990	0.0470
		Day 28	0.0390	0.0120	0.0340
Cabbage Santa Barbara	2	Day 1	0.4600	0.7200	0.4700
		Day 7	0.0020	0.0010	0.0007
		Day 14	0.0160	0.0420	0.0300
		Day 19	0.1200	0.1600	0.0930
		Day 21	0.1700	0.0990	0.0470
		Day 28	0.0390	0.0120	0.0340
Cabbage Santa Barbara	3	Day 1	0.9000	0.6800	0.7300
		Day 7	0.0180	0.0130	0.0080
		Day 14	0.0008	0.0010	0.0020
Broccoli Monterey	10	6 Hours	0.5800	0.9300	0.9100
		Day 1	1.0900	1.1100	NS
		Day 5	0.6700	0.6900	1.0400
		Day 14	0.0620	0.0650	0.0630
		Day 26	0.0320	0.0190	0.0490
Broccoli Monterey	19	6 Hours	3.2700	4.3500	4.6200
		Day 1	2.1100	1.7200	2.1100
		Day 2	2.8400	1.5700	2.9600
		Day 7	2.2100	2.6400	LS
		Day 14	0.6000	0.9600	1.0000
Cauliflower Monterey	18	Pre-applic.	0.0000	NS	NS
		6 Hours	2.3400	2.8100	2.5600
		Day 1	2.2700	1.1300	2.3000
		Day 2	2.1400	2.6900	2.9500
		Day 7	1.2900	0.9300	0.8100
		Day 14	0.0990	0.2900	0.0820
		Day 28	0.1520	0.0030	0.0390
Tomatoes Colusa	101	Day 8	0.8540	1.2100	0.6970
		Day 14	0.6140	NS	NS
		Day 21	1.0700	NS	NS
Tomatoes Colusa	102	Day 8	2.2300	1.7900	1.4900
		Day 14	0.6690	1.1700	0.4840
		Day 21	1.6600	NS	NS
Tomatoes Colusa	103	Day 3	0.3030	0.1520	1.0200
		Day 6	0.3800	0.3270	2.9500
		Day 8	0.2620	0.1680	0.8270
Celery Orange	3000	Pre-applic.	0.0015	0.0012	0.0014
		2 Hours	5.1300	4.4100	6.2300
		Day 1	5.2700	3.9600	5.0800
		Day 7	0.5600	1.1000	1.1200
		Day 13	0.5200	NS	NS
		Day 21	0.5400	0.1800	0.1800
		Day 28	ND	ND	ND

Appendix (Continued)

Crop/ County	Field Number	Sampling Interval	Replicate A	B	C
Celery Orange	5000	Pre-applic.	1.5500	1.8100	1.0000
		2 Hours	4.3700	3.4100	3.2000
		Day 1	5.4900	4.6100	3.1000
		Day 7	2.7800	2.7800	3.2200
Celery Orange	5001	Pre-applic.	2.7800	2.7800	3.2200
		2 Hours	5.6300	5.6300	NS
		Day 1	6.1700	NS	NS
		Day 5	4.1600	4.5600	6.2100
		Day 14	2.6500	3.2500	2.0100
Celery Orange	9000	Pre-applic.	0.6100	0.8700	0.5400
		2 Hours	3.6500	5.0800	4.5800
		Day 1	6.9600	6.2300	5.2200
		Day 5	4.4000	2.2500	4.1500
		Day 14	1.6700	1.0700	2.5300
		Day 21	0.1600	0.2700	0.2600
		Day 28	0.1300	0.1500	0.1700

ND - None detected, below 0.00038 ug/cm^2 minimum detectable level.
LS - Lost during extraction process or lost during shipping.
NS - No sample taken.